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<b>(54) Title:</b> POLYMERIC OPTICAL AMPLIFIER DOPED WITH LANTHANIDE		
<b>(57) Abstract</b> <p>The invention relates to a polymeric optical amplifier doped with lanthanide ions, which are present in the amplifier in the form of a complex. The invention also relates to novel electrically neutral lanthanide complexes which can be applied with advantage in the above-described polymeric optical amplifiers. These complexes comprise host molecules which readily complex with the lanthanide and fully encapsulate it.</p>		

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## POLYMERIC OPTICAL AMPLIFIER DOPED WITH LANTHANIDE

The invention relates to an optical amplifier doped with lanthanide ions. Such an optical amplifier is known from EP-A2-0 437 935, which describes an optical amplifier composed of an erbium<sup>3+</sup> doped fibre. The erbium ions are excited with the aid of a laser, giving a fibre containing a large number of excited Er<sup>3+</sup> ions. When optical beams (photons) having the same wavelength as the emission wavelength of the excited Er<sup>3+</sup> ions traverse the fibre, they effect the transition of the ions from the excited state to a lower energy level with transmission of light. As has been mentioned, this light will have the same wavelength and phase as the photons traversing the fibre. Such a process is called stimulated emission. In this way the light beams are amplified, with the optical fibre acting as amplifier.

The optical amplifier as specified in EP-A2-0 437 935 is a glass fibre. For several years efforts have been made in the industry to replace optical glass fibres with optical polymeric material. Optical polymeric fibres have several advantages over optical glass fibres. They can be made by less complicated spinning processes and can easily be cut to the required size and attached to receiving and transmitting devices. Also, they are lighter and more flexible than glass fibres. An attendant advantage is that the shape of optical polymeric material need not be restricted to fibres. The polymeric material can also be shaped into so-called flat waveguides. In the remainder of the description the term optical waveguides refers to both fibres and flat waveguides.

So far, it has not proved possible to replace lanthanide doped optical amplifiers with optical amplifiers of polymeric material. This is because polymeric waveguides cannot be doped with lanthanides just like that, without introducing co-doping with water. For, trivalent lanthanide ions are highly hygroscopic. In consequence, when lanthanide ions are doped, water of crystallisation which is present

into a polymeric optical fibre in a permanently anhydrous state in the form of a complex, without the advantages of polymeric optical fibres over glass fibres being attacked. In this way a lanthanide doped polymeric optical amplifier is provided which has all the above-mentioned advantages of polymeric optical waveguides to boot.

5 All lanthanide ions can be incorporated into polymeric optical waveguides in the form of a complex. Notably suitable are praseodymium (Pr), neodymium (Nd), europium (Eu), terbium (Tb), erbium (Er),  
10 thulium (Tm), and ytterbium (Yb). For instance, an optical waveguide into which  $\text{Pr}^{3+}$  and/or  $\text{Nd}^{3+}$  is incorporated in the complexed form is suitable for amplifying light of a wavelength of 1,3 micrometers. An optical waveguide into which  $\text{Er}^{3+}$  is incorporated in the complexed form can be used to amplify light of a wavelength of 1,5 micrometers. Light beams of these wavelengths (1,3 and 1,5 micrometers) are used in  
15 telecommunications systems because losses of signal in this wavelength range are minimal. (This wavelength range is a so-called optical window). Optical amplifiers doped with  $\text{Eu}^{3+}$  can be used for the amplification of red light, while optical amplifiers doped with  $\text{Tb}^{3+}$  serve to amplify green light.

20 When optical lanthanide doped waveguides are co-doped with  $\text{Yb}^{3+}$ , the ytterbium ion is excited. This excited  $\text{Y}^{3+}$  ion can transfer its energy to the lanthanide ion, which will be excited in its turn. Such a transfer of energy can also take place in the case of co-doping with  
25  $\text{Pr}^{3+}$ ,  $\text{Ne}^{3+}$ , and  $\text{Tm}^{3+}$ . The advantage here is that, since these lanthanides have absorption bands at different wavelengths, the selection of the type of laser to be used in the exciting process becomes less subject to restriction.  $\text{Tm}^{3+}$ , for instance, has an absorption band at 810 nanometers and so can be excited with a  
30 solid-state laser, while for  $\text{Er}^{3+}$  a different type of laser would be required. The ytterbium ion has a strong absorption band at 1000 nanometers, rendering it more readily excitable than, say, the erbium ion.

$(\text{CH}_2)_x\text{-O-P(=O)OH(OR}_9\text{)}$ ,  $\text{-(CH}_2\text{)-O-P(OR}_9\text{)}_3$ ,  
 $\text{-(CH}_2\text{)}_x\text{-O-POH(OR}_9\text{)}_2$ ,  $\text{-(CH}_2\text{)}_x\text{-O-P(=O)H(OR}_9\text{)}$ ;

x

is an integer from 0 to 3;

R<sub>7</sub>, R<sub>8</sub>

may be the same or different and represent:

$\text{-C(=O)-O-R}_{10}$ ,  $\text{-C(=O)-COOH}$ ,  $\text{-CH(=O)-COOR}_{10}$ ,  
 $\text{-C(=O)-NR}_{10}\text{R}_{10}$

5

may jointly, forming a cyclical compound,  
 represent:  $\text{-CH}_2\text{-O-(CH}_2\text{-CH}_2\text{-O-)}_n\text{-CH}_2\text{-}$ ,

$\text{-(CH}_2\text{-N(R}_{10}\text{)-CH}_2\text{)}_{n+1}\text{-}$ ,

$\text{-C(=O)-NR}_{10}\text{R}_{11}\text{-NR}_{10}\text{-C(=O)-}$ ,

$\text{-C(=O)-O-R}_{11}\text{-O-C(=O)-}$ ;

10

n

is an integer from 0 to 3;

R<sub>9</sub>

is an alkyl group having 1 to 3 carbon atoms  
 or a phenyl group;

R<sub>10</sub>

is an alkyl group or alkenyl group having 1  
 to 50 carbon atoms;

15

R<sub>11</sub>

is an alkyl group having 2 to 8 carbon atoms;

wherein the term alkyl group or alkenyl group refers to  
 branched as well as linear groups.

20

These novel compounds belong to a group generally known as  
 hemispherands. A major advantage of these novel hemispherands is that  
 metal ions are incorporated by deprotonation of the acid groups. In  
 the case of R<sub>4</sub>, R<sub>5</sub> and/or R<sub>6</sub> representing ester groups, they may be  
 deprotonated after saponification. The resulting tri-anion can form a  
 neutral complex with a lanthanide<sup>3+</sup> ion. Thus a neutral complex is  
 25 formed without a counterion being required as it is with conventional  
 ligand complexes. Given that charged particles as a rule are  
 objectionable in optical waveguides, where they may cause additional  
 losses of signal, this is of importance. These hemispherands are  
 eminently suitable compounds for complexing with lanthanides, since  
 30 they strip off all of the water on the lanthanide ion. Every  
 lanthanide can be incorporated into these novel hemispherands  
 according to formula 1. Praseodymium (Pr), neodymium (Nd), europium  
 (Eu), terbium (Tb), erbium (Er), thulium (Tm), and ytterbium (Yb) are  
 suitable for use in all of the above-described applications.

When the lanthanide complexes are incorporated into non-linear optical (NLO) polymers, the waveguides may be used as active units in optical circuits. For a more detailed explanation about the action of NLO polymers reference is made to C.B. McArdle (Loctite (Ireland) Ltd.), ed., Side Chain Liquid Crystal Polymers, Glasgow and London: Blackie, pp. 330-356. The combination of an amplifier and a circuit in a single waveguide makes it possible to have small-size intricate circuits. Also, loss of optical signal caused by switching on and off can be compensated for in this way. Special advantages can be gained by employing the novel neutral lanthanide complexes according to the present invention in NLO polymers. It is of importance not to have any charged particles in NLO optical waveguides. They give rise to drift during the waveguide's orientation and during switching, thus disturbing the switching action of the active unit. Using the electrically neutral lanthanide complexes according to the invention precludes the introduction of charged particles into the waveguide.

Alternatively, of course, lanthanide-doped NLO polymeric fibres can be employed solely as waveguide, without use being made of the non-linear optical properties of the polymer. Examples of NLO polymers that can be used include polyurethanes, polyesters, polyacrylates, and polymers derived from epoxides.

The invention will be further illustrated with reference to several unlimitative examples.

#### EXAMPLES

Synthesis of hemispherands according to formula 1: (For the formulae of the compounds and the reaction mechanisms readers are referred to the schedule.)

Compound 5

To a solution of compound 4 (18,9 g) in a mixture of 100 ml of MeOH and 100 ml of THF was added NaBH<sub>4</sub> (1,45 g), with the temperature being kept below 20°C. The reaction mixture was poured into 400 ml of ethyl acetate and twice washed with brine. The organic layer was dried with MgSO<sub>4</sub>, after which the salts were removed by filtration. The filtrate was condensed by evaporation and purified with the aid of column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane (1:3)), after which compound 5 was obtained as a clear oil in 82% yield (based on compound 3).

Compound 6

To a solution of compound 5 (16,36 g) in 150 ml of dry toluene under an atmosphere of nitrogen PBr<sub>3</sub> (6,50 g) was added dropwise at room temperature. After 45 minutes 200 ml of ethyl acetate were added. The organic layer was washed with, successively, brine (2 x), NaHCO<sub>3</sub>aq (1 x), and brine (1 x). After drying with MgSO<sub>4</sub>, filtering off of the salts, and concentration by evaporation the residue was purified with the aid of column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:2)). Compound 6 was obtained as a clear oil in 61% yield.

Compound 7a.NaClO<sub>4</sub>

A solution of compound 6 (5,38 g, 8,59 mmoles) and diethylene glycol (0,91 g, 8,59 mmoles) in 100 ml of THF was added to a refluxing suspension of 4 mol. of NaH (0,83 g) in 400 ml of THF over a period of 10 hours. The reaction was performed under a dry nitrogen atmosphere. After the addition was completed the reaction mixture was refluxed for an additional 3 hours, after which it was cooled to room temperature. Subsequently, 10 ml of water were carefully added to neutralise the remaining NaH. After evaporation of the THF the residue was dissolved in a mixture of MeOH and CH<sub>2</sub>Cl<sub>2</sub> (100 ml; 1:1) and 1 eq. of NaClO<sub>4</sub>.H<sub>2</sub>O in 10 ml of MeOH was added. This mixture was concentrated to

Compound 8a

5 A mixture of compound 7a, NaClO<sub>4</sub> (3.82 g, 3.98 mmol), 5 mole% Pd(OAc)<sub>2</sub>, 20 mole% Ph<sub>3</sub>P, 3 mol. eq. of Et<sub>3</sub>N, and 3 mol. eq. of HCOOH in 100 ml of EtOH and 20 ml of water was refluxed for one hour. The resulting mixture was cooled to 5°C to give 8a as precipitation. It was filtered off and dried in a vacuum oven at 80°C. The crude product (90%) was almost pure on the NMR scale and was used without further treatment.

Compound 8b

10 A mixture of compound 7b (3.00 g, 4.07 mmol), 5 mole% Pd(OAc)<sub>2</sub>, 20 mole% Ph<sub>3</sub>P, 3 mol. eq. of Et<sub>3</sub>N, and 3 mol. eq. of HCOOH in 50 ml of EtOH and 10 ml of water was refluxed for one hour. The resulting mixture was cooled to 10°C to give 8b as precipitation. It was  
15 filtered off and dried in a vacuum oven at 80°C. The crude product (80%) was almost pure on the NMR scale and was used for further reactions without additional treatment. A sample was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered over some silica gel. The silica gel was washed  
20 with some ethyl acetate and the combined organic layers were concentrated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and boiled in the presence of activated carbon. After filtration the organic layer was concentrated and the off-white residue recrystallised from acetonitrile to give compound 8b as white powder.

Compound 8c

25 A mixture of compound 7c (3.61 g, 4.40 mmol), 5 mole% Pd(OAc)<sub>2</sub>, 20 mole% Ph<sub>3</sub>P, 3 mol. eq. of Et<sub>3</sub>N, and 3 mol. eq. of HCOOH in 50 ml of EtOH and 10 ml of water was refluxed for one hour. The resulting mixture was cooled to 10°C to give 8c as precipitation. It was  
30 filtered off and dried in a vacuum oven at 80°C. The crude product (93%) was almost pure on the NMR scale and was used for further reactions without additional treatment. A sample was dissolved in a

Compound 9c

A mixture of compound 8c (2,65 g, 3,78 mmoles), ethyl bromoacetate (10 mol. eq.),  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (15 mol. eq.) and  $\text{K}_2\text{CO}_3$  (10 mol. eq.) was refluxed in 100 ml. of acetonitrile for 10 hours, after which it was cooled to room temperature. The salts were filtered off and washed once with acetonitrile. The combined organic layers were concentrated to dryness and some  $\text{CH}_2\text{Cl}_2$  was added. The resulting precipitation was filtered off and the filtrate concentrated. The product was purified by column chromatography ( $\text{SiO}_2$ , ethyl acetate) to give compound 9c. $\text{NaClO}_4$  as an oil that still contained a little ethyl bromoacetate. The latter may be removed in the next step.

Compound 10a

A mixture of compound 9a. $\text{NaClO}_4$  (0,30 g, 0,36 mmoles) in 5 ml of THF and 0,70 ml of 2,7 M  $\text{Me}_4\text{N}^+\text{OH}^-$  in water was stirred at room temperature for several hours until no starting material and only one new spot were present on TLC.

Subsequently, some water was added and acidified with 1 M HCl solution to pH=1-2. The aqueous phase was extracted once with ethyl acetate. After drying with  $\text{MgSO}_4$  the organic layer was concentrated to give compound 10a (90% yield) as a foam which was pure on the NMR scale.

Compound 10b

To a solution of compound 9b. $\text{NaClO}_4$  (2,45 g, 2,46 mmoles) in 30 ml of THF and 3 ml of water 13,2 ml of 2,7 M  $\text{Me}_4\text{N}^+\text{OH}^-$  in water were added and the resulting two-phase system was stirred for four days at room temperature.

Subsequently, 50 ml of water were added, followed by acidifying with 1 M HCl solution to pH=1-2. The aqueous layer was extracted once with 150 ml of ethyl acetate. The organic layer was washed twice with brine and concentrated. The residue was stripped with toluene, after which it was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered to give a clear solution. This



Europium complex 11b (M = Eu)

The crude product was dissolved in warm DMSO and after the addition of some vol. eq. of CH<sub>3</sub>CN the complex precipitated overnight (36%). Mp 270°C (decomposition). IR (KBr) 1659 and 1631 (C=O) cm<sup>-1</sup>.

5

Terbium complex 11b (M = Tb)

The crude product was treated in the same way as the corresponding europium complex (27%). Mp 270°C (decomposition).

10

Erbium complex 11b (M = Er)

No suitable solvent or mixture of solvents was found for the purification of the pale pink complex (87%). Mp 260°C (decomposition).

15

Europium complex 11c (M = Eu)

The crude product was purified by treatment with boiling CH<sub>3</sub>CN, after which the complex was obtained in 51% yield. Mp 230°C (decomposition). IR (KBr) 1660 and 1630 (C=O) cm<sup>-1</sup>.

20

Terbium complex 11c (M = Tb)

The crude product was purified by treatment with boiling CH<sub>3</sub>CN, after which the complex was obtained in 53% yield. Mp 225°C (decomposition).

25

Erbium complex 11c (M = Er)

The crude product was purified by treatment with boiling ethanol, giving the complex as a pale pink solid in 65% yield. Mp 240°C (decomposition).

30

Compound 15

Compound 14 (3,57 g, 4.26 mmol) was hydrolysed in a mixture of 50 ml of MeOH and 15 ml of 15% NaOH<sub>aq</sub>. After the reaction was completed according to TLC, 300 ml of water were added. The aqueous phase was acidified with 4 M HCl<sub>aq</sub> to pH=1 followed by extraction with 100 ml of ethyl acetate. The organic layer was washed once with brine and dried with MgSO<sub>4</sub>. After filtering off of the salts the filtrate was concentrated to give compound 15 as a colourless compound in quantitative yield.

Incorporation of lanthanides in acyclic hemispherand (cf. schedule, compound 16)

Compound 16

To a solution of compound 15 in MeOH 3 mol.eq. of 2,7 M Me<sub>4</sub>N<sup>+</sup>OH<sup>-</sup><sub>aq</sub> were added. To the resulting mixture a solution of 1 mol eq. of MCl<sub>3</sub>·6H<sub>2</sub>O (M= Eu, Tb, Er) or a solution of 1 mol eq. of Gd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in MeOH was added. The organic solvent was removed and some water was added. In the case of M= Eu, Gd, and Tb the complex was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried with MgSO<sub>4</sub> and concentrated after filtering off of the salts. In the case of M= Er, the resulting pale pink complex was filtered off, washed once with water, and dried in a vacuum oven (80 °C).

Ad Eu:

The europium complex was obtained as a practically white solid (85%). A solution (CH<sub>2</sub>Cl<sub>2</sub>, MeOH, THF, etc.) of the europium complex displays red luminescence from excitation with UV light ( $\lambda_{\text{max}}$  = 366 nanometers). This is also observed for the complex in the solid phase.

Ad Gd:

The gadolinium complex was purified by precipitation from a THF solution with the aid of n-hexane. The gadolinium complex was obtained as a white solid in a yield of 62%.

## SCHEDULE 1/3

5

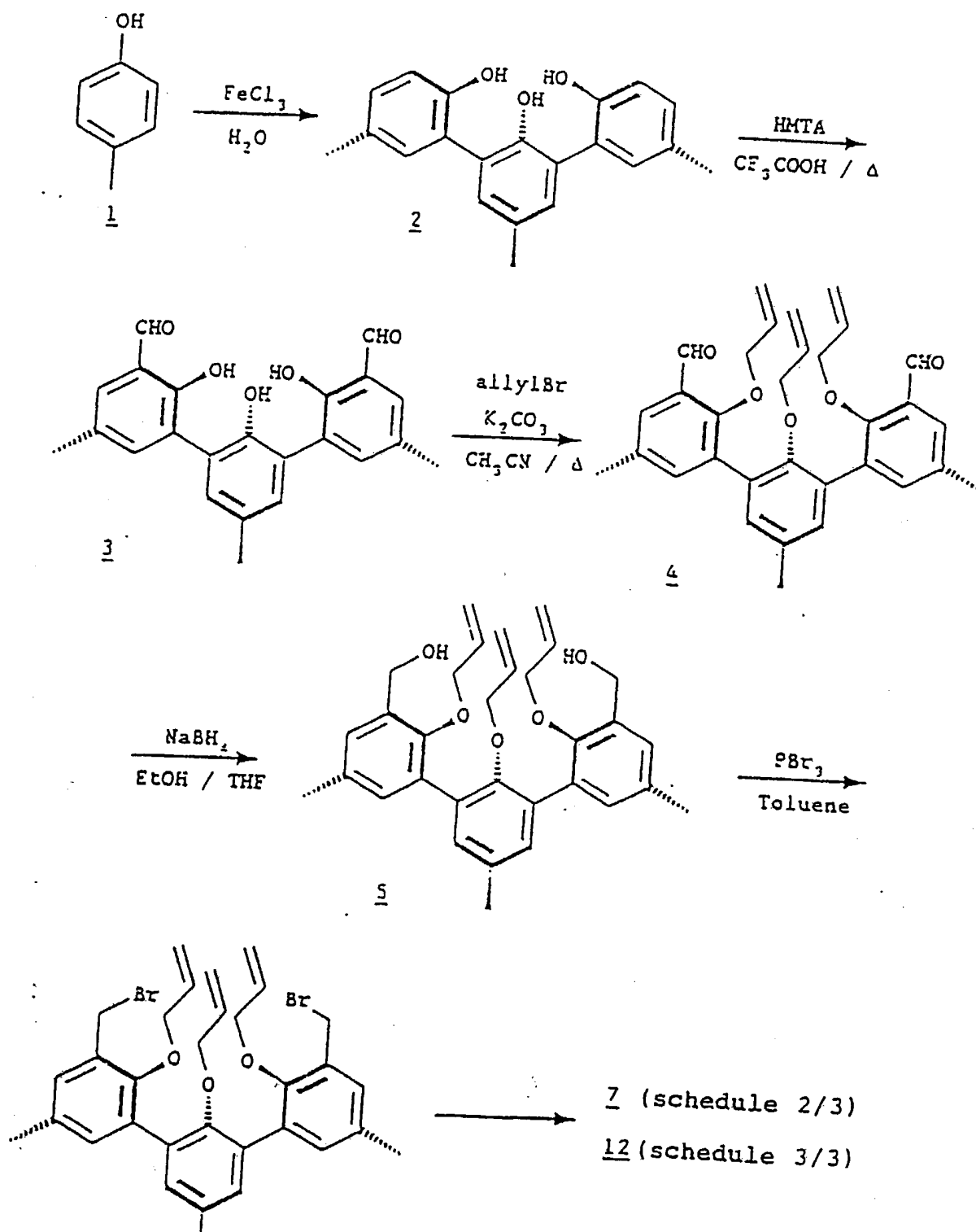
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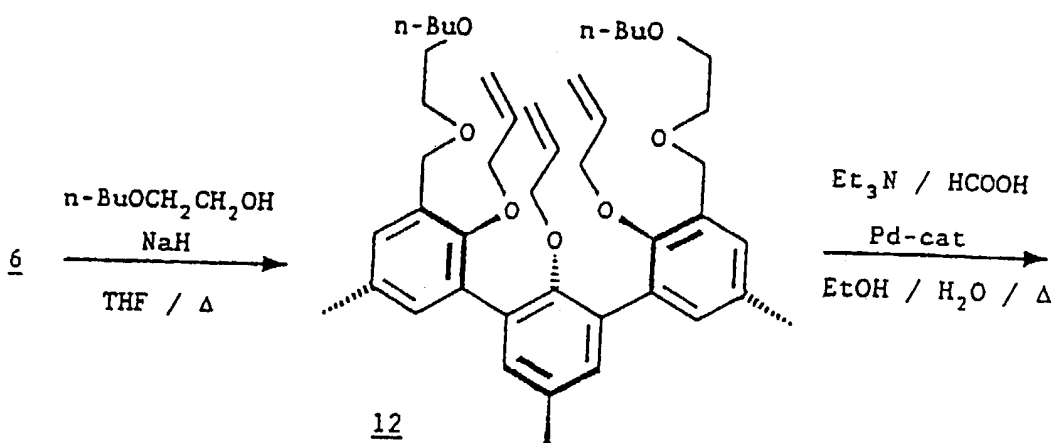
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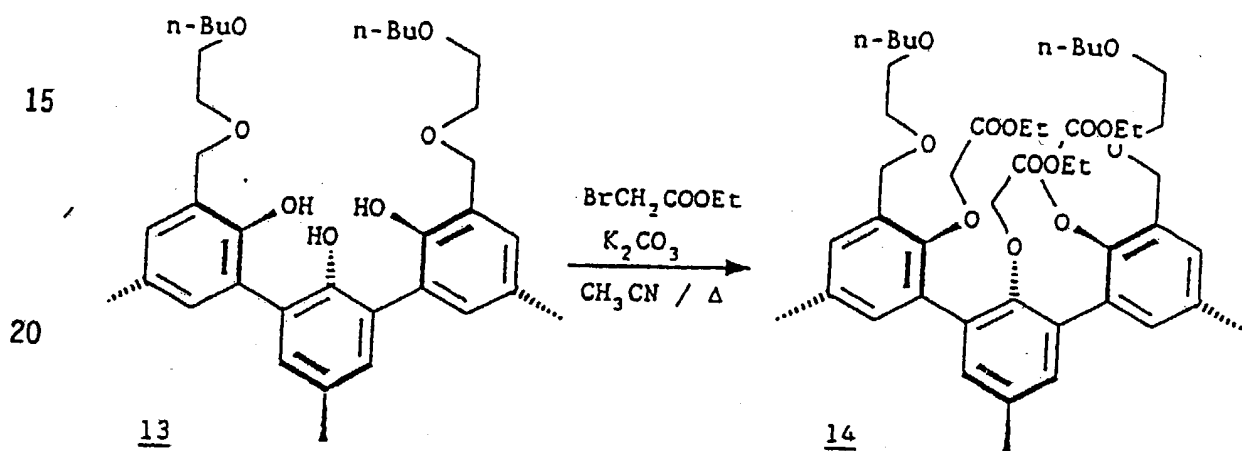


## SCHEDULE 3/3

5



10



15

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25

- 1)  $\text{OH}^-$
  - 2)  $\text{H}^+$  ( $\rightarrow$  15)
  - 3)  $\text{OH}^-$
  - 4)  $\text{MX}_3 \cdot n\text{H}_2\text{O}$
- $\xrightarrow{\text{MeOH}}$

30

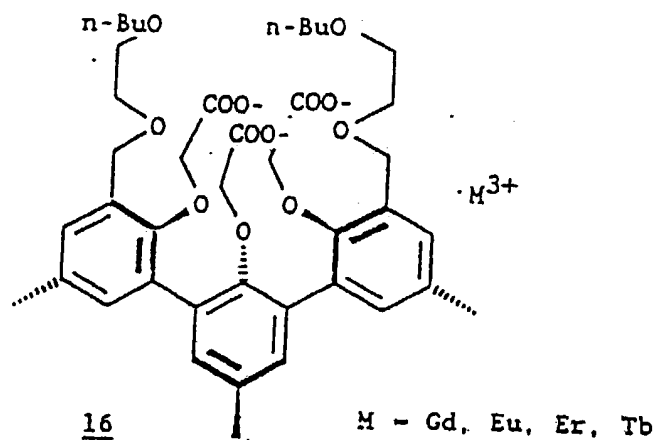


TABLE I

Compound	Concentration (M)	$\lambda_{exc.}$	$I_{MeOD}$	$I_{MeOH}$	$I_{MeOD}/I_{MeOH}$
		(nm)	( $\times 10^4$ )	( $\times 10^4$ )	
EuCl <sub>3</sub>	10 <sup>-3</sup>	393	87,5	7,4	11,8
		295	68,6	6,6	10,4
		266	67,3	5,7	11,8
16, M=Eu	10 <sup>-3</sup>	393	62,8	14,6	4,3
		295	313,4	86,8	3,6
		266	47,1	11,3	4,2
11b, M=Eu	10 <sup>-3</sup>	393	6,3	6,2	1,0
		295	15,7	12,7	1,2
		266	-	-	-

10

The results depicted in TABLE I show that the luminescence of EuCl<sub>3</sub> in deuterated methanol is much higher than in methanol. This illustrates the quenching by OH-groups of the excited state in EuCl<sub>3</sub>. From the fact that the luminescence intensity is reduced much less in complexes according to the invention when using methanol instead of deuterated methanol, it can be concluded that the lanthanide ions are very well shielded by the hemispherand.

Further, luminescence emission and excitation spectra were measured on an acyclic Tb<sup>3+</sup> complex (compound 16) and an acyclic Eu<sup>3+</sup> complex (compound 16) in a thin film of PMMA. The luminescence spectra of both the Eu<sup>3+</sup> and the Tb<sup>3+</sup> complex in PMMA were exactly the same as those obtained in solution, which indicates that the same species are present in both matrices.

25

Luminescence emission and excitation spectra were measured of an acyclic Er<sup>3+</sup> complex (compound 16) in deuterated methanol. Both excitation at 275 nm and at 980 nm resulted in luminescence in the 1530 nm region.

30

- 50 carbon atoms, an alkenyl group having 1 to 50 carbon atoms, a halogenated alkyl group having 1 to 50 carbon atoms, -C(O)H, -COOH, -O-R<sub>10</sub>, -O-R<sub>10</sub>-OH, -R<sub>10</sub>-OH, -COOR<sub>10</sub>, COOR<sub>10</sub>-C(O)H, -COOR<sub>10</sub>-COOH, O-R<sub>10</sub>-NH<sub>2</sub>, -R<sub>10</sub>-NH<sub>2</sub>, -NO<sub>2</sub> or an amine group;
- 5 R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> may be the same or different and represent: -(CH<sub>2</sub>)<sub>x</sub>COOH, -(CH<sub>2</sub>)<sub>x</sub>COOR<sub>9</sub>, -(CH<sub>2</sub>)<sub>x</sub>SO<sub>3</sub>H, -(CH<sub>2</sub>)<sub>x</sub>SO<sub>3</sub>R<sub>9</sub>, (CH<sub>2</sub>)<sub>x</sub>-O-P(O)(OR<sub>9</sub>)<sub>2</sub>, 10 (CH<sub>2</sub>)<sub>x</sub>-O-P(O)OH(OR<sub>9</sub>), -(CH<sub>2</sub>)<sub>x</sub>-O-P(OR<sub>9</sub>)<sub>3</sub>, -(CH<sub>2</sub>)<sub>x</sub>-O-POH(OR<sub>9</sub>)<sub>2</sub>, -(CH<sub>2</sub>)<sub>x</sub>-O-P(O)H(OR<sub>9</sub>);
- x is an integer from 0 to 3;
- 15 R<sub>7</sub>, R<sub>8</sub> may be the same or different and represent: -C(O)-O-R<sub>10</sub>, -C(O)-COOH, -CH(O)-COOR<sub>10</sub>, -C(O)-NR<sub>10</sub>R<sub>10</sub> may jointly, forming a cyclical compound, represent: -CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>n</sub>-CH<sub>2</sub>-, 20 -(CH<sub>2</sub>-N(R<sub>10</sub>)-CH<sub>2</sub>)<sub>n+1</sub>-, -C(O)-NR<sub>10</sub>R<sub>11</sub>-NR<sub>10</sub>-C(O)-, -C(O)-O-R<sub>11</sub>-O-C(O);
- n is an integer from 0 to 3;
- R<sub>9</sub> is an alkyl group having 1 to 3 carbon atoms or a phenyl group;
- 25 R<sub>10</sub> is an alkyl group or an alkenyl group having 1 to 50 carbon atoms;
- R<sub>11</sub> is an alkyl group having 2 to 8 carbon atoms;
- 30 wherein the terms alkyl group and alkenyl group refer to branched as well as linear groups.

5. An optical amplifier according to any one of the preceding claims, characterised in that the polymeric optical waveguide comprises a non-linear optical polymer.

may jointly, forming a cyclical compound,  
represent:  $-\text{CH}_2-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_2-$ ,  
 $-(\text{CH}_2-\text{N}(\text{R}_{10})-\text{CH}_2)_{n+1}-$ ,  
 $-\text{C}(\text{O})-\text{NR}_{10}\text{R}_{11}-\text{NR}_{10}-\text{C}(\text{O})-$ ,  
 $-\text{C}(\text{O})-\text{O}-\text{R}_{11}-\text{O}-\text{C}(\text{O})$ ;

n is an integer from 0 to 3;

R<sub>9</sub> is an alkyl group having 1 to 3 carbon atoms or a phenyl group;

R<sub>10</sub> is an alkyl group or an alkenyl group having 1 to 50 carbon atoms;

R<sub>11</sub> is an alkyl group having 2 to 8 carbon atoms;

wherein the terms alkyl group and alkenyl group refer to branched as well as linear groups.